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# THE CORROSION OF SOME STAINLESS STEELS IN A MARINE MUD.

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## ABSTRACT.

The report presents the results for three alloys; carbon steel, 316L stainless steel and the authors' company's proprietary super duplex stainless steel (UNS S32760)*, exposed in a marine mud off the south coast of England for 5 years. Analysis of the mud showed it to be very aggressive using a corrosion index developed at the University of Manchester. Carbon steel showed a typical corrosion rate for microbial attack with pits up to 0.64mm deep. The 316L stainless steel had extensive broad, shallow attack with a few, deeper pits. The Z100 parent pipe and weldments showed no evidence of corrosion attack.

Keywords: Marine Corrosion, MIC, Stainless Steel.

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* The alloy is referred to by the generic name Z100 hereafter.

## INTRODUCTION

It is well known that carbon steel corrodes in sea water and also suffers from microbially induced corrosion (MIC) when exposed to biologically active muds[1]. The desire to mitigate this effect has resulted in trials of stainless steels such as 316L, but MIC of this alloy has been reported in a variety of service environments. Z100 super duplex stainless steel has excellent resistance to crevice corrosion and pitting in sea water [2,3]. It has been used for sea water pumps since 1986 and for piping in sea water systems since 1989, with excellent results. With the increasing exploitation of the ocean resources, there is an increasing requirement to understand the performance of materials in subsea muds, eg. for piling, subsea flowlines etc, and a long term study of corrosion in sea water mud has been undertaken. The aim of the research is to examine both general and localised corrosion in marine mud, and whether microbiological corrosion (MIC) will occur. This report presents the results of specimens exposed for 5 years.

## EXPERIMENTAL

### Site

To ensure that MIC would occur it was necessary that specimens be exposed at a marine site, buried in mud known to be rich in bacteria. The site chosen was the mud flats adjacent to the Hayling Yacht Company, Hayling Island, Hampshire, UK, as shown in Figure 1. These flats are submerged under about 1 metre of water around high tide, but are uncovered for several hours around low tide. There is approximately 300mm of black mud on the surface with a mixture of clay, stone and sand beneath. The mud is biologically active with a strong smell when disturbed.

### Materials

All of the test materials were in seamless pipe form, and the sizes are shown below:

| Ref No. | Alloy | | Form |
|---|---|---|---|
| OC9761 | Carbon Steel | - | 2½ NPS Sched 40 |
| OC9762 | 316L Stainless Steel | - | 1½ NPS Sched 40S |
| OC9763 | Z100 Super Duplex | - | 2 NPS Sched 40S (girth welded) |
| OC9764 | Z100 Super Duplex | - | 2 NPS Sched 40S (plain) |

The carbon steel was included to assess the general aggressiveness of the environment, and 316L stainless was selected as an alloy which is known to be susceptible to crevice corrosion in aerated sea water. The super duplex stainless steel was Zeron 100 (1), manufactured by Weir Materials & Foundries. The increasing use of the alloy in dockside applications led to its inclusion in the present tests. A sample of Z100 pipe with a GTAW girth weld in the centre was included as welds are often thought to be more susceptible to MIC. The pipe was exposed in the as-welded condition. The nominal compositions of the stainless steels are shown in Table 1.

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(1) registered trademark of Weir Materials & Foundries,

Exposure Condition

Two types of exposure were examined. The first consisted of short lengths of pipe (~ 0.5m long) driven vertically into the mud with only 20 to 30 mm exposed above the mud line. A hole was drilled near the top of the pipe and a rope was tied from the pipe to a hardwood frame anchored in the mud to aid relocation. Two samples of each material were exposed in this manner initially, with further samples being added as others were removed. The Z100 specimens had a girth weld (GTAW) half way along, as described above. It was originally intended that the pipes be fully submerged but the movement of the surface mud, described below, meant that a short length at the top of the pipe was frequently exposed to water. However, this is exactly what can happen to a subsea pipeline laid in mud and so the exposure was felt to represent service conditions.

To provide test conditions under which pipes were exposed continuously to sea water above the mud line, three 0.9 m lengths of 150 mm diameter plastic pipe were driven vertically into the mud for half their length to retain sea water when the tide went out and a 1.2 m length of plain Z100 pipe was driven down into the mud at the centre of each. A wooden framework retained the plastic and Z100 pipes in position. Under this arrangement the lowest 600mm of each test pipe was below the mud line, the next 450mm was continuously submerged and the top 150 mm was submerged for three or four hours around high tide but exposed to the atmosphere the rest of the time. This type of exposure is similar to that seen by risers in the oil and gas industry. Photographs of the test rig at low and three quarter high tide are shown in Figure 2.

The exposures commenced in June 1992. One or two specimens that were fully immersed in mud were removed after 6 months and one-year exposure. These were hosed down to remove deposits, visually examined on site, photographed and then re-buried. After two years one of each of the fully buried specimens and one of the half - buried samples was removed for detailed examination. The same selection of samples was removed in 1997, after 5 years' exposure.

## ASSESSMENT OF THE MUD

Four samples of mud were taken by CAPCIS in May of 1996, and these were tested for sulphate reducing bacteria (SRB), sulphides, organics, nitrogen and phosphorus. The results are shown in Table 2.

The greater the SRB count the more aggressive the mud is potentially. Farhina (3) looked at a selection of muds from around the UK coast, plus several others. The most aggressive had a summer SRB count of $10^7$ cells/ml. The SRB figures in Table 2 are typical for UK muds and similar to those observed by Farhina [4].

However the SRB count alone does not give a complete indication of the likely severity of microbial corrosion. King [5] produced a ranking table taking a number of factors into account. However, Farhina [4] found this inadequate for UK marine muds and proposed a modified ranking system. This takes into account the nature of the sediment, the organic content, the availability of nitrogen and phosphorus, the temperature and the sulphate content. Table 3 shows the factors in Farhina's index and the weighting attached to each one for different concentrations. The availability of N and P is classed as high when N>1% and P>0.3% of the dried weight. Farhina's index correlated well with the corrosion rate of carbon steel at 9 different locations. A mild mud with an index of 4 gave a corrosion rate of 15µm/year, while an aggressive mud with an index of 15 gave a corrosion rate of 312µm/year. The four samples taken at Hayling Island all gave indices of 12, which shows them to be "more aggressive than average", based on Farhina's data, as shown in Table 3.

The conclusion of this examination is that the mud at Hayling Island is very active biologically and very likely to cause microbial corrosion.

## EXAMINATION

Carbon Steel (OC 9761)

There was heavy general corrosion along the full length of the pipe, both inside and out. In addition there was some pitting attack as shown in Figure 3. The pitting was deeper and more widespread on the outside surface of the pipe. Some pits were broad and others were narrow but most were of similar depth. At the mudline there was a whitish, crystalline deposit, which tested positively for carbonate.

The corrosion products were a mixture of orange and black deposits. Some of the black product was clearly magnetic, but it also gave a positive reaction to the sodium azide test for sulphides. Hence the corrosion products are presumed to be a mixture of FeOOH, $Fe_3O_4$ and FeS.

The wall thickness was measured on a number of sections to make an estimate of the general corrosion rate. The mean of twenty readings was 4.57mm ( + 0.48 and - 0.37). This meant a metal thickness loss of 0.59 mm or 0.12 mm/year. This assumes a linear loss of metal with time. Even with carbon steel this is not strictly true and corrosion rates tend to decrease with time, as the corrosion products hinder access of reactants to the metal surface [1]. However, the metal loss was from two surfaces. If the corrosion was at the same rate inside and out the mean corrosion rate was 0.06 mm/year. However, the appearance suggested a greater rate of corrosion outside than in. If the rate is arbitrarily taken as twice as great on the outside compared with the inside, a corrosion rate of 0.08 mm/year was occurring on the outside.

The depths from ten typical pits were measured as shown in Table 4. The results show that a maximum depth of 0.64mm i.e. a pit penetration rate of ~ 0.13 mm/year, should be added to the general corrosion rate. This assumes a linear rate of penetration which is not strictly true, as rates tend to decrease with time.

### 316L Stainless (OC9762)

There was no attack on the inside of the pipe. Pitting near the location of the hole was attributed to crevice corrosion, possibly between the anchoring rope and the pipe, in open sea water. At the mudline there was a ring of crystalline deposits which tested positive for carbonates.

There were patches of general corrosion all over the external surface. In some places this was very rough and widespread, while in others the areas of attack were only a few millimetres across in an otherwise unattacked surface. A typical example is shown in Figure 4.

There were pits all over the external surface of the pipe, with a total count of approximately 15. The depths of the ten deepest are shown in Table 4, which also shows the average depth to be 0.27 mm. The maximum pit depth was 0.37mm i.e. an annual pit propagation rate of 0.07mm/y, assuming a linear propagation rate. As for carbon steel this is not strictly true as penetration rates tend to decrease with time. A typical pit, Figure 5, shows the pit bottom was smooth and approximately hemispherical. Any corrosion products must have been loosely adherent as they washed out during cleaning of the pipe.

### Welded Z100 (OC9763)

There was no corrosion on the inside or the outside of the pipe. At about the position of the mudline there was a crystalline deposit which tested positive for carbonate. No attack could be found either under or adjacent to this deposit.

Comparison of the surface condition of exposed and unexposed Z100 pipes shows that original extrusion marks were retained on the pipe surface as shown in Figures 6 and 7.

There was no attack associated with either the girth weld or its associated heat affected zone.

### Plain Z100 (OC9764)

This pipe showed lots of weed and green slime at the water line. Beneath this growth was a crystalline deposit which tested positive for carbonate. There were silty deposits on the outside of the pipe down to the mudline, but no corrosion on either the inside or outside of the pipe. Again, original pipe extrusion marks could be found on the pipe surface similar to those in Figures 6 & 7.

# DISCUSSION

The nature of the corrosion products on the carbon steel pipe (OC9761) and the analysis of the mud, indicate that the mud at Hayling Island is biologically very active. The corrosion rate of carbon steel in aerated sea water is 0.11 to 0.15 mm/year [1]. The results show that microbial corrosion of the carbon steel is clearly occurring with a corrosion rate of half to two thirds of that in open, aerated sea water. However, the presence of pits as well means that the penetration rate could be more rapid than in open sea water.

Microbial corrosion of carbon steel in anaerobic marine muds is usually due to the presence of sulphate reducing bacteria which reduce the sulphate present in the sea water to sulphide.

The fact that corrosion products other than FeS were observed suggests that corrosion is not simply by the anodic reaction of iron with hydrogen sulphide,

i.e. $Fe + H_2S \rightarrow FeS + H_2$

Instead the production of oxides and hydroxides would also be expected if the cathodic reaction involved the reaction (5),

$$4Fe + 4H_2O + SO^{2-}_4 \rightarrow 3\,Fe(OH)_2 + FeS + 2OH^-$$

The exact mechanism during microbial corrosion is far from simple, as enzymes can catalyse some reactions [1]. However, the present results are typical for microbial attack of carbon steel [4]. Farhina observed corrosion rates of steel piling in UK marine muds from 0.04 to 0.1 mm/y.

The appearance of the 316L stainless steel suggests that breakdown of the passive film occurred at many sites, but it only developed into full scale pitting at a small number of sites.

Corrosion of stainless steels is usually localised, and occurs where the passive film has broken down. Rapid corrosion of the exposed metal occurs because of the large cathode to anode area ratio. The stability of the passive film is reduced by the addition of chloride or other halide ions to the water because they are able to penetrate the passive film. Once a pit has initiated the anodic reaction generates metal ions at the bottom of the pit. These become hydrolysed and free hydrogen ions are generated resulting in a lowering of the pH in the pit. Electrical neutrality is maintained in the pit by the migration of halide ions into the pit. Thus, the micro-environment in the pit becomes concentrated in chloride ions and lower in pH than the bulk solution. These conditions help to prevent repassivation of the pit so that once started, pits will tend to propagate unless they become so large that the opening collapses and the pit environment is washed out by the bulk liquid.

The only significant microbially induced corrosion mechanism of stainless steels [6] is the production of reduced sulphur compounds (such as sulphide and thiosulphate) by the activities of sulphate-reducing bacteria (SRB). However, slime forming bacteria (called heterotrophs) often play a physical role of providing an environmental niche on the metal substrate, beneath which the SRB can proliferate. The reduced sulphur compounds produced by SRB can induce chloride pitting attack at potentials hundreds of millivolts more negative than would otherwise be the case. This is because the sulphur compounds stabilise metastable pitting induced by halides. Metastable pits are those that repassivate after growing only a few µm deep. Active halide corrosion inside a tight crevice can be similarly stabilised. Sulphide and thiosulphate act as very effective sources of absorbed sulphur for pit initiation. They are charged anions and are therefore enriched in pit nuclei; (i.e. in metastable pits) by electromigration and are readily reduced on the metal surface, yielding sulphur:

e.g. $S_2O_3^{2-} + 6H^+ + 4e \rightarrow 2\,S_{ads} + 3H_2O$

Thus, under optimum conditions, biogenic pitting may occur near the lowest potential where metastable pitting occurs in $S_2O_3^{2-}$ - free solutions. The by-product of SRB metabolism converts metastable pits into stable, propagating pits.

This mechanism suggests that microbial attack of 316L, and other low alloy stainless steels should produce narrow deep pits. However, the broad, shallow attack observed in the present tests suggests that although pits did initiate, they were also able to repassivate. A possible reason for this is the instability of the mud bank where the samples were buried. After every visit it was noticeable that the upper layers of mud, up to 150 mm or so had moved, sometimes increasing the depth of mud, sometimes the reverse. This movement of mud would almost certainly have introduced some dissolved oxygen which would react with the sulphur compounds and result in repassivation of the stainless steel. The surface of the 316L stainless suggests that pit initiation and repassivation occurred numerous times, and only in a few cases were stable, propagating pits established.

It could be argued that the corrosion was caused not by MIC but be differential aeration, i.e. the upper part of the pipe in aerated sea water formed the cathode, while the lower portion of the pipe in deaerated mud formed the anode. This is not thought to be the case for the carbon steel because, if this mechanism was operating, more of the pitting would be expected close to anode/cathode boundary, and this was not the case. However, it is probable that differential aeration did play a part in the corrosion of the 316L pipe. Stainless steels are frequently used in sour oil and gas fluids containing substantial quantities of $H_2S$ and pitting does not occur on 316L at ambient temperature (e.g. NACE TM0177). Hence the presence of $H_2S$ from SRB's is unlikely to have caused the observed pitting even if the local pH was reduced.

However, a differential aeration cell would provide a more efficient cathodic reaction, i.e. the reduction of dissolved oxygen. The role of the $H_2S$ would then be to increase the likelyhood of breakdown at film defects (7). Hence the attack on the 316L could perhaps be regarded as microbially induced differential aeration corrosion. This suggests that corrosion would be unlikely on fully buried 316L. It is also not clear how important the $H_2S$ is to this kind of attack, and it would be interesting to conduct tests in a mud with a much lower bacterial activity.

From an engineering point of view the broad, shallow attack on the 316L was of no significance. However, the pitting of 316L is of significance where perforation is an issue, e.g. submerged piping.

The Z100 super duplex stainless steel showed no evidence of corrosion attack on either the parent pipe or welds. Several studies [8, 9] have shown that weld metal and heat tints from welding operations are sites which are more susceptible to microbial attack than parent metal. However, these studies have been on 300 series stainless steels The weld on the Z100 pipe showed no such susceptibility and the weld metal and HAZ were free of all signs of corrosion.

## CONCLUSIONS

1. The mud at Hayling Island is biologically very active.
2. Carbon steel was corroding at 0.06 to 0.08 mm/year with a maximum pit depth, after five years, of 0.64 mm.
3. 316L stainless steel suffered broad shallow attack below the mud line with a few, deeper, propagating pits. The greatest pit depth was 0.37 mm.
4. Z100 super duplex stainless steel showed no evidence of corrosion attack in either the pipe , weldmetal or the heat affected zone.
5. There was no corrosion of the Z100 super duplex stainless steel in aerated sea water, even under weed and slime deposits, or at the mudline.

## ACKNOWLEDGEMENTS

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## Table 1 Nominal composition of the stainless steels

| ALLOY | Ref No. | NOMINAL COMPOSITION (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Fe | C | Cr | Ni | Mo | N | Cu | W |
| 316L | OC9762 | bal | 0.02 | 17 | 11 | 2.2 | - | - | - |
| Z100 | OC9763 | bal | 0.02 | 25 | 7 | 3.5 | 0.25 | 0.7 | 0.7 |
| Z100 Welded | OC9764 | bal | 0.02 | 25 | 7 | 3.5 | 0.25 | 0.7 | 0.7 |

bal = balance

# Table 2 Results of the mud analyses

| SAMPLE | MEAN SRB* (Cells/g) | MEAN SULPHIDE+ (ug/g) | ORGANIC CONTENT# (% dry wt.) | NITROGEN CONTENT$ (% dry wt.) | PHOSPHORUS CONTENT** (% dry wt.) |
|---|---|---|---|---|---|
| Centre Offshore | 1,000 | 1,000 | 13 | >1 | >0.3 |
| Debris from Plastic Pipe | 10,000 | 400 | 11 | >1 | >0.3 |
| Centre Landward | 10,000 | 4,300 | 15 | >1 | >0.3 |
| End of Frame | 1,000 | 3,500 | 14 | >1 | >0.3 |

* By serial dilution
\+ By ion chromatography
\# By pyrolysis at 550°C
$ By Kjeldahl method
** By vanadomolybdate method

# Table 3 Ranking index of harbour muds from Farhina (ref 3)

| FACTOR | SCORE | HAYLING ISLAND RANKINGS | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| Nature of sediment | | | | | |
| a) mud | 2 | 2 | 2 | 2 | 2 |
| b) sand/mud | 0 | | | | |
| Organic content (%wt) | | | | | |
| If mud >15 very high | 4 | | | | |
| 10 - 15 high | 3 | 3 | 3 | 3 | 3 |
| 5 - 10 medium | 2 | | | | |
| <5 low | 0 | | | | |
| If sand | 0 | | | | |
| Availability of N and P | | | | | |
| If high a) High organic content | 3 | 3 | 3 | 3 | 3 |
| b) Medium organic content | 2 | | | | |
| c) Low organic content | 0 | | | | |
| If low | 0 | | | | |
| Temperature | | | | | |
| >15°C | 3 | | | | |
| 5° - 15°C | 2 | 2 | 2 | 2 | 2 |
| <5°C | 0 | | | | |
| Sulphate | | | | | |
| >1000 mg/l | 3 | | | | |
| 500 - 1000 mg/l | 2 | 2 | 2 | 2 | 2 |
| 200 - 500 mg/l | 1 | | | | |
| <200 mg/l | -1 | | | | |
| TOTAL SCORE | | 12 | 12 | 12 | 12 |

# Table 4 Depths of pits on fully buried sections of pipe

| ALLOY | Ref No. | DEPTH (mm) | MEAN (mm) |
|---|---|---|---|
| Carbon Steel | OC9761 | 0.50;0.60;0.23;0.14<br>0.27;0.46;0.36<br>0.46;0.64;0.50 | 0.42 |
| 316L | OC9762 | 0.23;0.10;0.24;0.23<br>0.32;0.31;0.36<br>0.37;0.25;0.29 | 0.27 |

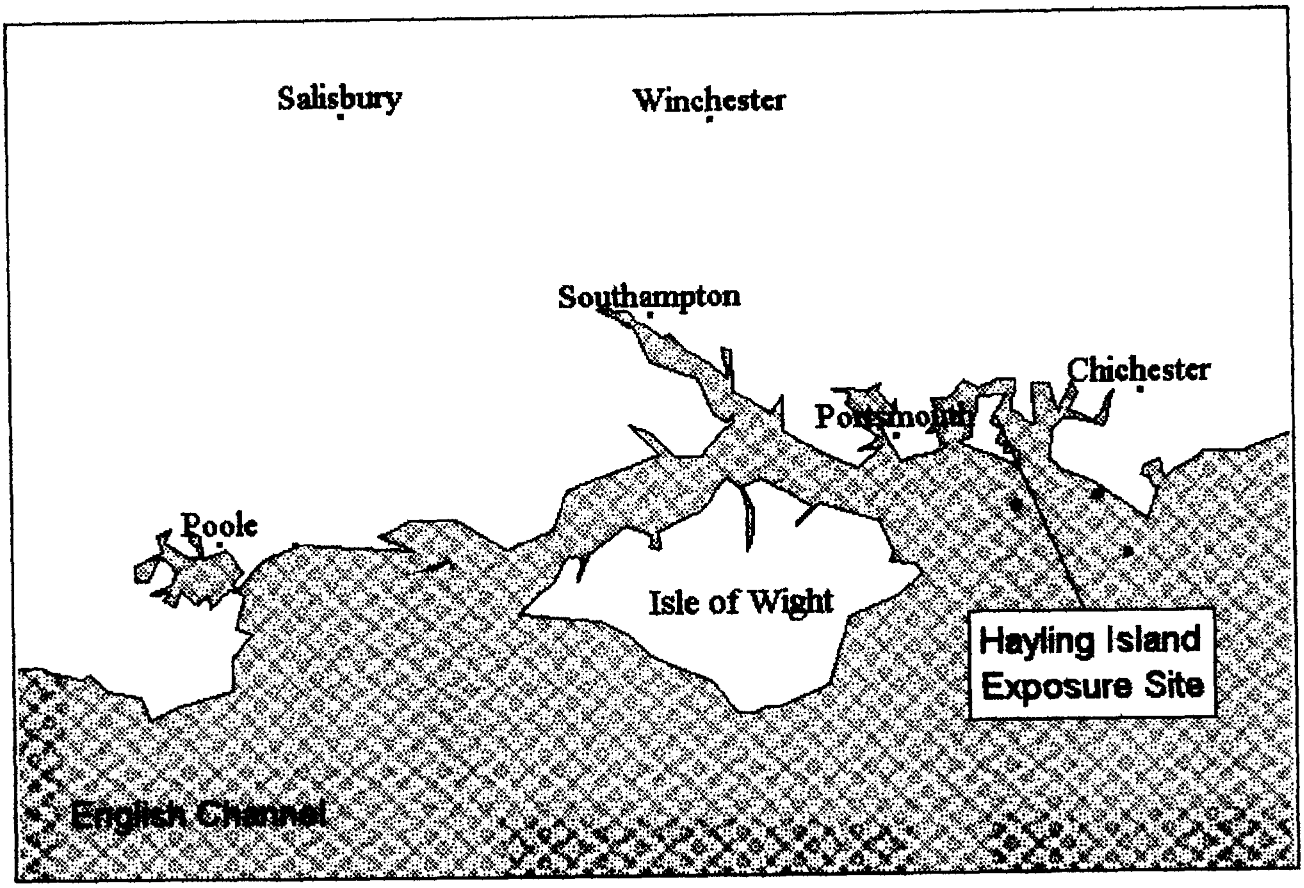
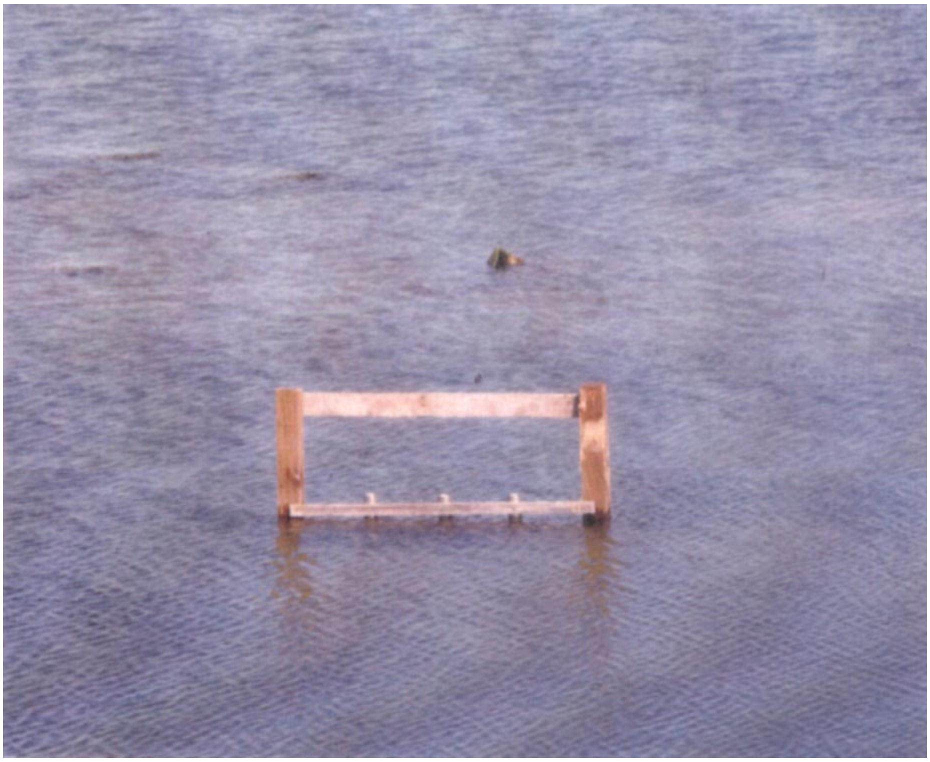


FIGURE 1 The location of the exposure site on the South coast of England.

(a) Low Tide



(b) Three quarters high tide

FIGURE 2. Views of exposure test ring at Hayling Island

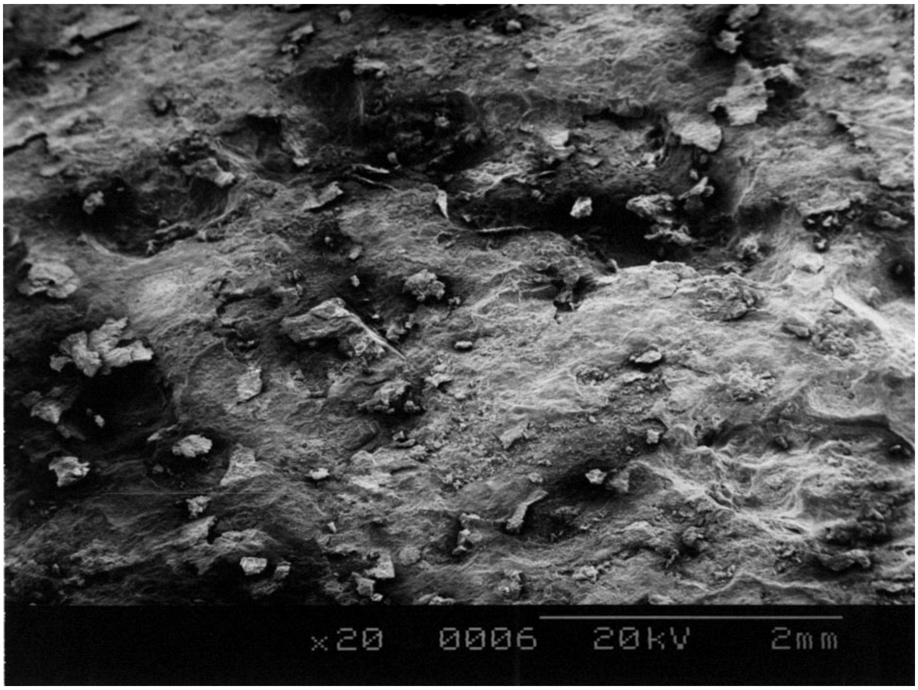


Figure 3 - Pits on external surface of carbon steel after 5 years' exposure.

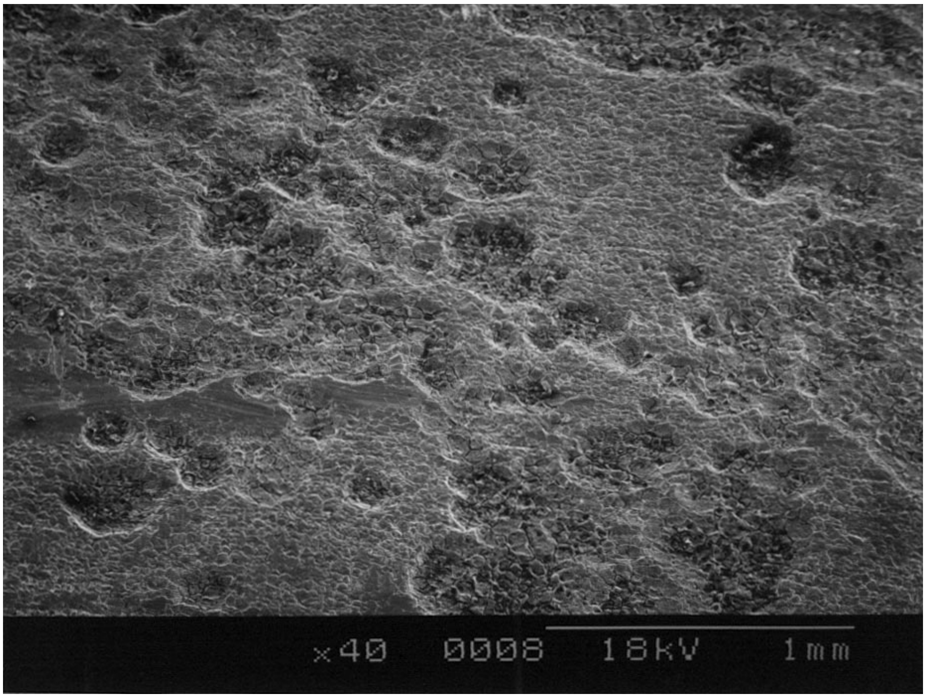


Figure 4 - General dissolution of 316L stainless exposed for 5 years.

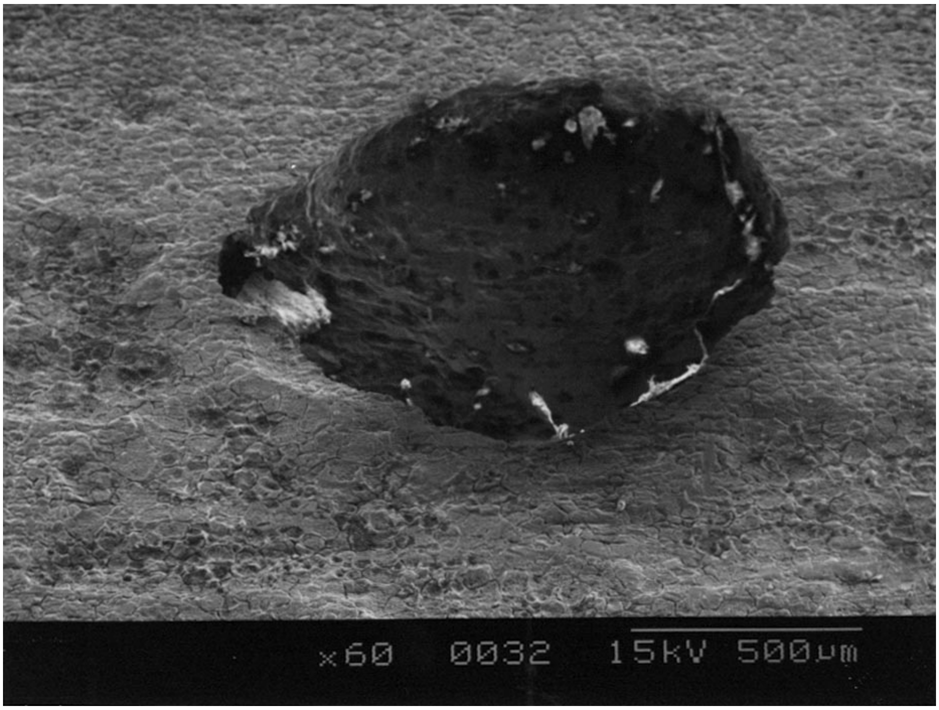


Figure 5 - Pitting on 316L stainless exposed for 5 years.

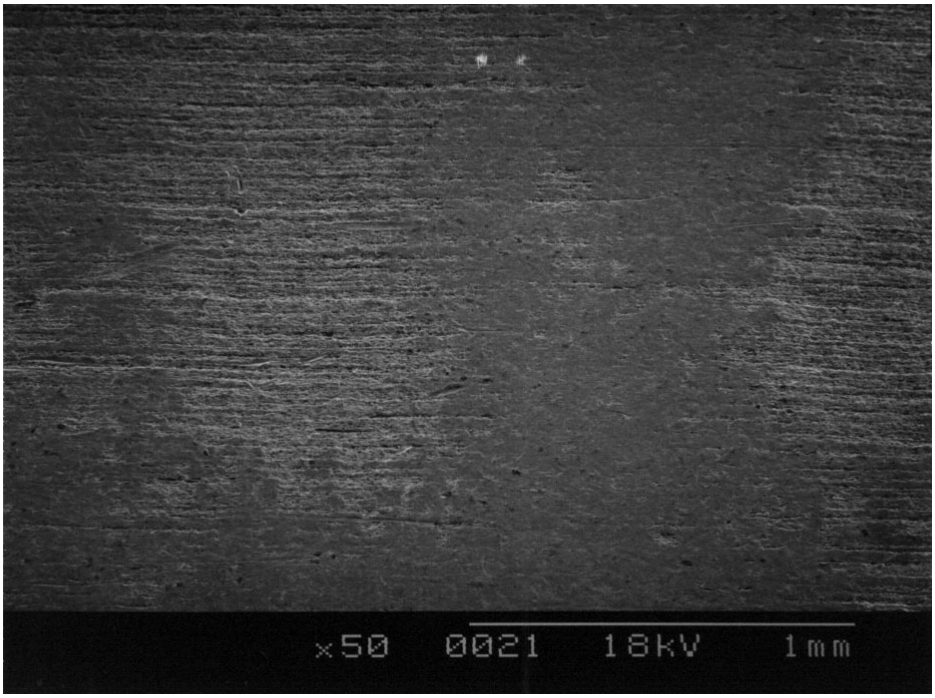


Figure 6 - Broad, shallow extrusion marks on Z100 still present after exposure for 5 years.

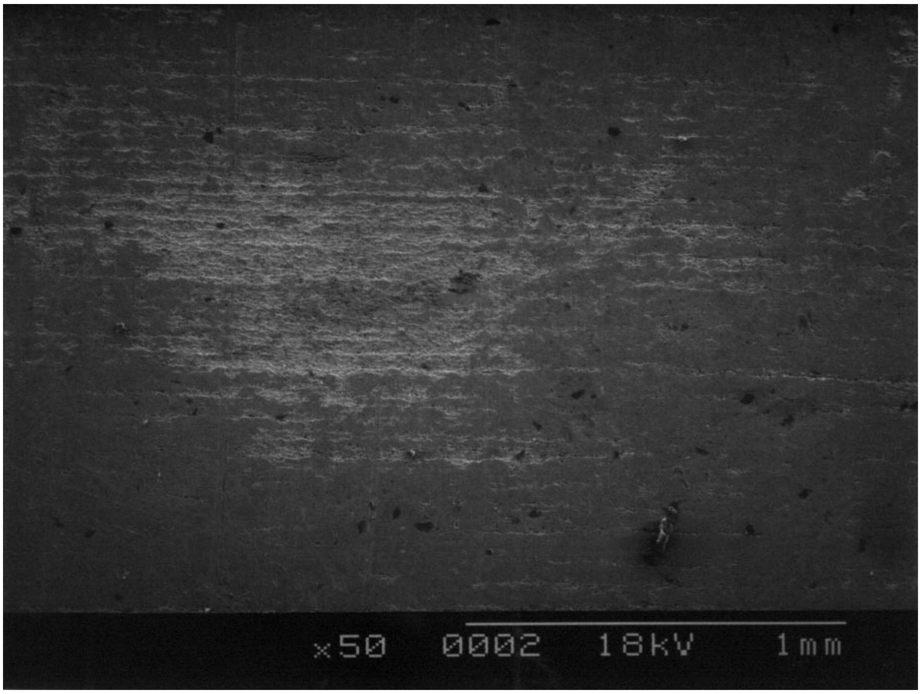


Figure 7 - Broad shallow extrusion marks on Z100 in the as-manufactured(unexposed) condition.